

The presence of metastable $\text{HNO}_3/\text{H}_2\text{O}$ solid phases in the stratosphere inferred from ER 2 data

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Abstract. We present data to show that at least some of the observed polar stratospheric cloud (PSC) particles sampled by the ER 2 on January 20, 1989, during the Airborne Arctic Stratospheric Expedition (AASE 1) were composed of a water-rich $\text{HNO}_3/\text{H}_2\text{O}$ solid phase. The PSC water content derived from the ER 2 data on this day is larger than that of nitric acid trihydrate (NAT), nitric acid dihydrate (NAD) or an aqueous ternary solution of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$. Here, we suggest that these particles were composed of a water-rich metastable $\text{HNO}_3/\text{H}_2\text{O}$ solid phase and refer to such clouds as Type 1c PSCs, which are different from Type 1a (crystalline NAT or NAD particles) or Type 1b (aqueous ternary solution droplets) PSCs. Type 1c PSCs could either be crystalline (a higher hydrate of HNO_3 and H_2O) or amorphous, and the data analysis presented here cannot distinguish between these different solid phases. The observed PSC on this day could have been a mixture of water-rich HNO_3 -containing solid particles with liquid ternary droplets and/or NAT (NAD) aerosols. However, a mixture of cloud particles composed of ternary solution droplets and NAT (NAD) aerosols is inconsistent with the data. A surface adsorption/reaction process occurring on frozen sulfate surfaces is suggested as a formation mechanism for Type 1c PSCs in the stratosphere. A possible mechanism for the formation of large HNO_3 -containing aerosols (NAT or NAD) starting with Type 1c PSCs is discussed.

Introduction

It was first suggested by Toon *et al.* [1986] and Crutzen and Arnold [1986] that HNO_3 may condense under polar winter stratospheric conditions, possibly in the form of thermodynamically stable HNO_3 trihydrate (NAT) [Toon *et al.*, 1986]. Later, the vapor pressure behavior of HNO_3 over NAT was established by laboratory studies [Hanson and Mauersberger, 1988]. Since the work of Hanson and Mauersberger [1988], the thermodynamics of NAT have been used commonly for predicting the onset temperature and composition of Type 1 PSC [e.g., Fahey *et al.*, 1989; Dye *et al.*, 1990; Hofmann and Deshler, 1990; Hofmann *et al.*, 1991; Dye *et al.*, 1992; Kawa *et al.*, 1992; Poeschel *et al.*, 1992; Rosen *et al.*, 1993]. However, during the Airborne Arctic Stratospheric Expedition (AASE I), large NAT supersaturations were routinely observed before significant particle growth was evident [e.g., Dye *et al.*, 1992]. Also, measurements of the HNO_3 mole content of the aerosols were consistently lower than that of NAT [Kawa *et al.*, 1992]. The lack of consistency between PSC observations and a NAT composition is not unique to Arctic PSCs. Recent interpretations of the Antarctic PSCs observed spectroscopically in September 1987 strongly suggest that these PSCs were not composed of NAT [Toon and Tolbert, 1995].

To resolve the discrepancies between assuming a NAT composition for Type 1 PSCs and observations, several investigators have suggested that the HNO_3 vapor pressure may be controlled by a different condensed phase of HNO_3 and

H_2O , and some have provided vapor pressure curves for such phases. The suggested compositions are aqueous HNO_3 solutions [Hanson, 1990], HNO_3 dihydrate (NAD) or HNO_3 decahydrate [Worsnop *et al.*, 1993], HNO_3 penta- or hexahydrate [Marti and Mauersberger, 1993, 1994], ternary solutions of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ [Arnold, 1992; Zhang *et al.*, 1993; Molina *et al.*, 1993; Tabazadeh *et al.*, 1994a, b; Carslaw *et al.*, 1994], and $\text{H}_2\text{SO}_4/\text{HNO}_3$ pentahydrate [Fox *et al.*, 1995]. All the suggested phases, except NAD, contain more H_2O than NAT and therefore are closer to the observed PSC compositions [Kawa *et al.*, 1992].

Recently, we found that the calculated aerosol mass for the AASE 1 ER 2 flight of January 24 agrees well with the observed cloud mass if a ternary solution composition is assumed for the particles [Tabazadeh *et al.*, 1994b; Drdla *et al.*, 1994]. However, the cloud mass obtained assuming a NAT or NAD composition for the cloud particles is inconsistent with the data. Other models for ternary solutions yield similar results [Carslaw *et al.*, 1994]. Of the eight AASE 1 ER 2 flights described by Dye *et al.* [1992] and Kawa *et al.* [1992] only the flights of January 24 and 25 are consistent with the presence of particles supporting the thermodynamics of liquid ternary solutions. The rest of the flights are inconsistent with the observed PSC particles being composed solely of ternary solution droplets or solid phases such as NAT or NAD. Here we describe the observations during one such flight.

Particle Composition and Vapor Pressure

Cloud particle volume and size [Dye *et al.*, 1992], NO_y [Kawa *et al.*, 1992], N_2O [Loewenstein *et al.*, 1990], temperature and pressure [Chan *et al.*, 1990], and H_2O vapor pressure [Kelly *et al.*, 1990] for the ER 2 flight of January 20 are used here to

derive a relation for the variation of the HNO_3 vapor pressure over the observed PSC cloud on this day. We used the data in the time period of 38500 to 41500 UT, where the cloud particles were observed. We did not use the data between 40500 to 41000 UT because the air was denitrified for this short time period [Kawa *et al.*, 1992; Dye *et al.*, 1992] and even though temperatures were cold enough to observe Type 1 PSCs, no enhancement in the cloud particle volume was measured. The N_2O values remained relatively constant during this time period, indicating that all the data points were perhaps taken in the same air mass [Loewenstein *et al.*, 1990].

For comparisons to the data, the vapor pressures of Hanson and Mauersberger [1988] were used for NAT and the vapor pressures of Worsnop *et al.* [1993] were used for NAD. For the determination of the HNO_3 vapor pressure over ternary solutions, the Aerosol Physical Chemistry Model (APCM) calculations were used [Tabazadeh *et al.*, 1994a; Jacobson *et al.*, 1996]. Briefly, the APCM is an equilibrium model, which calculates the composition of stratospheric aerosols that are in thermal equilibrium with the respective vapors (HNO_3 and H_2O) for an assumed mass of condensed H_2SO_4 .

Aerosol HNO_3 Content

We have used relations derived by Fahey *et al.* [1989] and Loewenstein *et al.* [1993] to distribute the total HNO_3 present in the air mass into the aerosol HNO_3 and the gas phase HNO_3 . To calculate a HNO_3 aerosol volume mixing ratio ($[\text{HNO}_3]_{\text{aer}}$) from Kawa *et al.*'s [1992] data, we used the equations derived by Fahey *et al.* [1989] for the ER 2 measurements. Assuming that all the condensed NO_y is HNO_3 ($[\text{NO}_y]_{\text{aer}} = [\text{HNO}_3]_{\text{aer}}$), the HNO_3 aerosol mixing ratio in units of parts per billion by volume is given as

$$[\text{HNO}_3]_{\text{aer}} = \frac{[\text{NO}_y]_{\text{meas}} - [\text{HNO}_3]_{\text{gas}} - (1-R)[\text{NO}_y]^*}{A_{\text{eff}}} \quad (1)$$

where $[\text{NO}_y]_{\text{meas}}$ is the total measured NO_y volume mixing ratio, and $[\text{HNO}_3]_{\text{gas}}$ is the equilibrium volume vapor mixing ratio of HNO_3 over the condensed HNO_3 phase. The amount of HNO_3 available for condensation is a fraction, R (we assumed $R = 0.9$), of available NO_y . The $[\text{NO}_y]^*$ is the total NO_y present in the air mass inferred from the N_2O measurement [Loewenstein *et al.*, 1993]. The A_{eff} is an enhancement factor which increases the observed particle NO_y by a factor of about 6 to 9 [Kawa *et al.*, 1992]. The A_{eff} values were calculated as described by Fahey *et al.* [1989]. The total HNO_3 present in the air mass is approximated from [Loewenstein *et al.*, 1993]

$$\begin{aligned} [\text{HNO}_3]_{\text{T}} &= [\text{HNO}_3]_{\text{aer}} + [\text{HNO}_3]_{\text{gas}} = R[\text{NO}_y]^* \\ &= R\{20.7 - 0.0644[\text{N}_2\text{O}]\} \end{aligned} \quad (2)$$

where $[\text{N}_2\text{O}]$ and $[\text{HNO}_3]_{\text{T}}$ are in parts per billion by volume. Solving (1) and (2) simultaneously yields the partitioning of HNO_3 between the aerosol and the gas phase, given as

$$[\text{HNO}_3]_{\text{aer}} = \frac{[\text{NO}_y]_{\text{meas}} - [\text{NO}_y]^*}{(A_{\text{eff}} - 1)} \quad (3a)$$

$$[\text{HNO}_3]_{\text{gas}} = R[\text{NO}_y]^* - [\text{HNO}_3]_{\text{aer}} \quad (3b)$$

Note that (3a) is independent of $[\text{HNO}_3]_{\text{gas}}$ and therefore we do not need to assume a composition for the condensed HNO_3 phase in order to compute $[\text{HNO}_3]_{\text{aer}}$. Further, the vapor pressure of the condensed HNO_3 phase can now be evaluated directly from (3b). Drdla *et al.* [1994] have presented similar analysis of the ER 2 data for the determination of $[\text{HNO}_3]_{\text{aer}}$. However, most of the previous analysis of the ER 2 data have set $[\text{HNO}_3]_{\text{gas}} = [\text{HNO}_3]_{\text{HM}}$ (where $[\text{HNO}_3]_{\text{HM}}$ is the vapor pressure of HNO_3 over NAT, in units of parts per billion by volume, calculated from Hanson and Mauersberger [1988a]) and calculated $[\text{HNO}_3]_{\text{aer}}$ from (1) instead of (3a) [Fahey *et al.*, 1989; Kawa *et al.*, 1992].

Figure 1 illustrates the distribution of HNO_3 into aerosol HNO_3 and gas phase HNO_3 for the ER 2 flight of January 20 calculated from (3a) and (3b). The calculated vapor pressure of the particles (Figure 2a) does not agree with either NAT or NAD, and is slightly different than what is predicted for supercooled ternary solutions (STS). If only the vapor pressure data is used, then ternary solutions, considering the uncertainties, can provide a reasonable fit to the data. The HNO_3 abundance in the aerosols (Figure 2b) independently shows that NAT or NAD compositions are inconsistent with the data. In most places the STS aerosol content is a factor of 2 to 5 lower than the derived HNO_3 aerosol mixing ratio from (3a). Also, for temperatures below 191 K, the HNO_3 mixing ratio for ternary solutions should be higher than the observations. Our results (Figure 2b) differ significantly from the previous analysis on this day (see Figure 3 of Kawa *et al.* [1992]), mainly because we are not assuming $[\text{HNO}_3]_{\text{gas}} = [\text{HNO}_3]_{\text{HM}}$, as described above.

It is interesting to note that the HNO_3 vapor pressure of the observed cloud particles are about 10 - 20 times higher than what is expected for the HNO_3 vapor pressure over NAT, as shown in Figure 2a. This high vapor pressure is consistent with a few laboratory measurements in which HNO_3 and H_2O were deposited on either glass or SAT [Hanson, 1992; Marti and Mauersberger, 1993; Iraci *et al.*, 1995]. The measured HNO_3 vapor pressure over the condensed $\text{HNO}_3/\text{H}_2\text{O}$ film deposited on a SAT layer in a flow tube were consistently higher than that calculated for NAT by a factor of 10 - 20 for a time period of at least 40 min [Hanson, 1992].

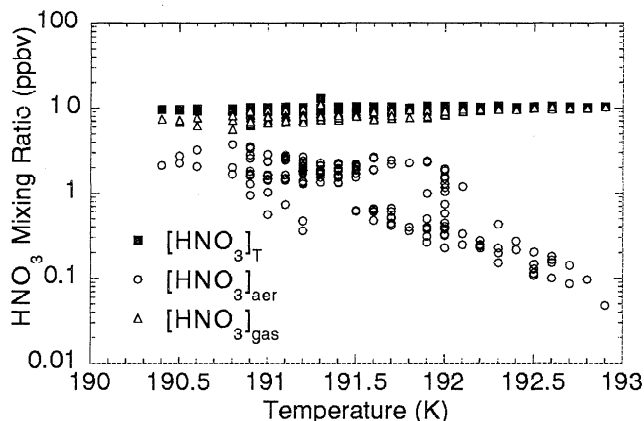


Figure 1. Variation of the total HNO_3 , gas phase HNO_3 and aerosol phase HNO_3 as a function of the ambient temperature for the ER2 flight of January 20 calculated from (3). See text for more detail.

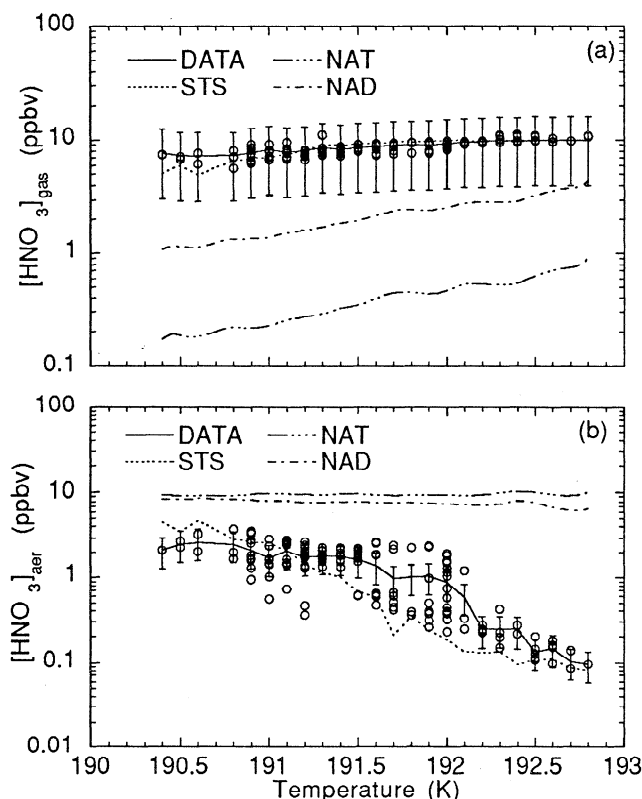


Figure 2. Variation of the (a) HNO₃ vapor pressure mixing ratio and (b) HNO₃ aerosol mixing ratio as function of the ambient temperature. STS refers to supercooled ternary solutions of H₂SO₄/HNO₃/H₂O. The solid line is calculated by averaging the data points shown in Figure 1 at every given temperature. NAT, NAD and STS values are calculated using the total HNO₃ mixing ratios given in Figure 1 along with the measured H₂O vapor concentration and the total pressure as described in the text. The measurement uncertainties are shown as error bars ($\pm 60\%$ and $\pm 40\%$ of the solid line for Figure 2a and 2b, respectively). See text for more detail.

Aerosol Volume

The FSSP 300 volume is plotted as a function of temperature in Figure 3. If ternary solutions are present, then the observed cloud volume should increase gradually with temperature decrease below 192 K. As shown in Figure 3, ternary solutions under equilibrium conditions can not explain the observed cloud volume. If ternary solutions are influenced by short time scale temperature fluctuations, then the cloud particles are not at equilibrium [Murphy and Gary, 1995]. For example, the volume growth could be caused by the presence of ternary solutions in the air mass that were at lower temperatures a short while ago and have not yet adjusted to the new temperatures. In principle, temperature fluctuations should result in cooling and warming with about equal frequency. However, it appears that roughly 95 % of the data points shown in Figure 3 contain more volume than expected for ternary solutions. This is inconsistent with a fluctuation scenario since 95 % of the data points would require cooling instead of a roughly 50 % split between cooling and warming. In addition, the ER 2 data of January 16 and 19 also indicate the presence of mainly regions higher in volume than expected for ternary solutions. Similarly, this would require more cooling in relation to warming. In sum, these observations may suggest that it is

unlikely for the condensed HNO₃ phase to have been composed entirely of ternary solution droplets on these 3 days since significantly more cooling episodes are needed to explain the occurrence of regions higher in volume than expected for ternary solutions.

The volume measured by the FSSP 300 can be explained if the observed cloud particles were composed of either NAT or NAD aerosols. However, this volume can be obtained only if most of the available HNO₃ is condensed along with the appropriate amount of H₂O. However, this scenario is inconsistent with the results shown in Figure 2b since the aerosols contained between 0.1 and 3 parts per billion by volume of HNO₃. The corresponding NAT or NAD volume obtained using the measured HNO₃ in the aerosols would result in calculated volumes that are lower than observed by a factor of 2 to 20 depending on the chosen temperature. This calculation shows that the presence of NAT or NAD particles even under nonequilibrium conditions is unable to explain the volumes measured by the FSSP 300. Hence the presence of NAT or NAD particles under either equilibrium or nonequilibrium conditions is inconsistent with both the particle volume and composition data for the ER 2 flight of January 20.

Aerosol Composition

To calculate an approximate aerosol composition, the FSSP 300 volume (shown in Figure 3) was converted into units of mass by first subtracting the SAT volume from the total measured FSSP 300 volume and then multiplying this subtracted volume by an average density. The SAT volume was set at $0.1 \mu\text{m}^3 \text{cm}^{-3}$, which corresponds approximately to one half of the averaged measured FSSP 300 volume in the air mass prior to the PSC observations and roughly agrees with the dry aerosol volume estimated by Wilson *et al.* [1992] (Note that the FSSP 300 only samples particles that are $> 0.2 \mu\text{m}$ in radius and therefore prior to a PSC event, the measured volume is always smaller than the actual volume because the majority of particles are below $0.2 \mu\text{m}$ [Baumgardner *et al.*, 1992]). The HNO₃ content of the aerosol was calculated from converting the mixing ratios shown in Figure 2b into units of mass.

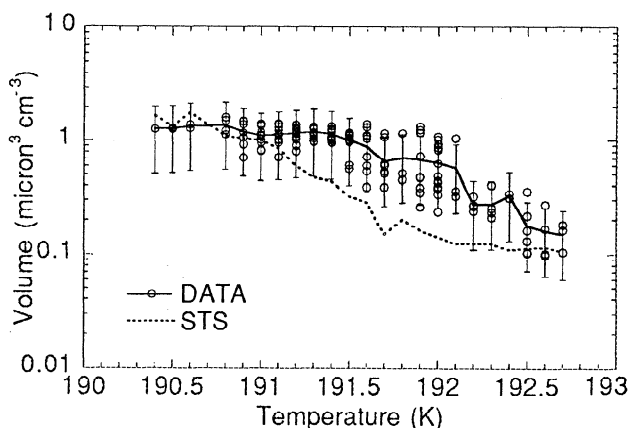


Figure 3. FSSP 300 volume as a function of the ambient temperature for the ER2 flight of January 20. The circles are the data points and the solid line is calculated by connecting the average values at every temperature. The ternary solution line is calculated as described in Figure 2. The measurement uncertainties are shown as error bars ($\pm 60\%$ of the solid line). See text for more detail.

Dividing the HNO_3 mass (Figure 2b) by the total mass (Figure 3), the weight fraction of HNO_3 can be calculated. The weight fraction of H_2O is then determined by subtracting 1 from the weight fraction of HNO_3 since we have previously subtracted the H_2SO_4 component.

In Figure 4, the water content of the aerosol is plotted as a function of the cloud temperature. Figure 4 shows that the water content of the cloud particles varied slightly with temperature. The calculated values suggest that the aerosols are more dilute in HNO_3 at higher temperatures. For the temperature range shown in Figure 3, ternary solutions should contain roughly 50 % H_2O by weight with very small variations in the H_2O content of the aerosol. However, in general, the water content of ternary solutions should increase with temperature decrease because of the increase in the relative humidity [Tabazadeh *et al.*, 1994a]. Also, aqueous HNO_3 solutions were stable only for $T < 191$ K as shown in Figure 4 (gray region) and most of the cloud mass was observed above 191 K. Thus the observed PSC particles were not entirely composed of an aqueous phase of HNO_3 either as a binary or as a ternary system.

The variation of the aerosol water content with temperature may indicate that the observed cloud particles were not composed of a single hydrate of HNO_3 and H_2O , where the composition of the aerosol is fixed. For air supersaturated with respect to HNO_3 , NAT (~ 46 % water by weight) or NAD (~ 36 % water by weight) aerosols should still maintain their HNO_3 to H_2O mole ratio. Every time a HNO_3 molecule is absorbed by the aerosol, the appropriate H_2O molecules are added and therefore the particle composition remains constant. Thus even though nonequilibrium conditions can explain the large NAT supersaturations observed during the AASE 1, the particle composition data clearly rules out any condensed $\text{HNO}_3/\text{H}_2\text{O}$ phase with a fixed mole ratio of HNO_3 to H_2O .

The number of H_2O molecules per HNO_3 in the solid phase varied from 5 to 16 as shown in Figure 4, which is different than that of NAT (3 H_2O molecules) or NAD (2 H_2O molecules). It is interesting to note that the presence of more dilute

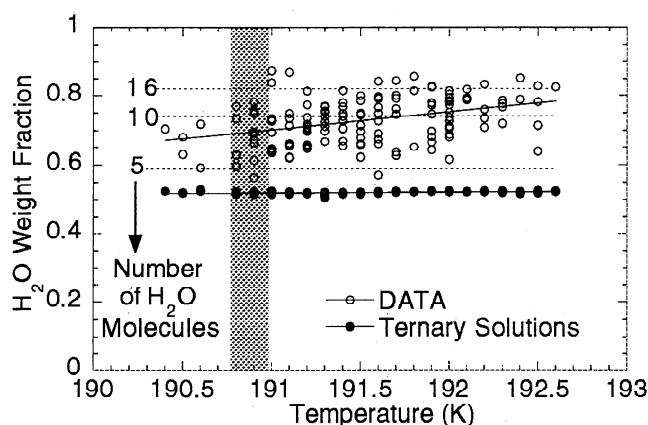


Figure 4. The water content of the observed cloud particles as a function of the ambient temperature for the ER2 flight of January 20. The open circles are the data points and the solid circles are the ternary solution values calculated using the in situ HNO_3 and H_2O vapor pressure and temperature. The variation of the number of H_2O molecules per HNO_3 in the solid phase is shown in the upper left-hand corner of the chart. The gray area illustrates the onset temperature range where aqueous binary HNO_3 solutions become stable.

hydrates of HNO_3 and H_2O has been reported in the literature, such as pentahydrate [Marti and Mauersberger, 1994], decahydrate [Worsnop *et al.*, 1993] and decahexahydrate [Pickering, 1893]. These higher hydrates of HNO_3 expand the derived compositional spectrum of the cloud particles on January 20 and therefore the PSCs observed on this day could have been composed of higher hydrates of HNO_3 (Figure 4). It is possible that a higher hydrate of HNO_3 and H_2O initially nucleated in the air mass and then aged gradually with time, by losing water and rearranging its structure, to grow richer in HNO_3 (see below). Since the concentrated hydrates of HNO_3 (NAT or NAD) have lower vapor pressures than the calculated vapor pressures of the observed PSC particles (see Figure 2a), the transformation from the higher to the lower hydrates of HNO_3 should be thermodynamically favorable.

The variation of the aerosol water content with temperature may have also been caused by the presence of a homogenous amorphous solid solution of HNO_3 and H_2O . The distinction between a crystalline (higher hydrates) or an amorphous solid phase of HNO_3 and H_2O cannot be inferred from the available data at this point.

The observed cloud particles may have also been a mixture of liquid and solid aerosols. The liquid particles could be ternary solutions and the solid particles could be a higher hydrate. This condition may occur if a fraction of sulfate cores are frozen into SAT. The frozen cores could grow into a higher hydrate and the liquid cores would grow to become ternary droplets. The calculated composition at every temperature should then depend on the volume fraction occupied by different particle phases. For example, the observed compositions shown in Figure 4 could be a mixture of ternary solutions and HNO_3 deca- or decahexahydrate. However, the observed particles could not have been a mixture of ternary solutions and NAT (or NAD) because the water weight percent of this mixture is always less than that of a ternary solution (~ 50 % H_2O by weight), which does not support the observed data (see Figure 4). The possibility that the observed cloud was a mixture of higher hydrate particles and NAT (or NAD) aerosols is described below.

Derived Particle Composition and Vapor Pressure

The particle composition can be calculated from the results shown in Figure 4 using

$$f_w = \frac{[\text{H}_2\text{O}]_T \{0.1027T - 18.1976\}}{1000[\text{HNO}_3]_T} \quad (4)$$

Here f_w refers to the water weight fraction of the aerosols, and $[\text{H}_2\text{O}]_T$ is the total water mixing ratio in units of parts per million by volume. We have chosen to use a vapor ratio of H_2O to HNO_3 because laboratory studies indicate that this ratio controls the mole percent of HNO_3 in the condensed $\text{HNO}_3/\text{H}_2\text{O}$ phase [Marti and Mauersberger, 1993]. However, the ambient water vapor did not vary enough on this day to confirm this dependence. To estimate the HNO_3 vapor pressure curve over this solid phase, the HNO_3 gas phase concentrations shown in Figure 2a were plotted against the composition data shown in Figure 4 at constant temperatures. The vapor pressure results are illustrated in Figure 5 for five selected temperatures. The temperature range of the data varied from 190.5 to 192.6 in increments of 0.1 K (Figures 2a and 4). The calculated vapor pressures were then grouped and fitted to a polynomial function in temperature and composition, given as

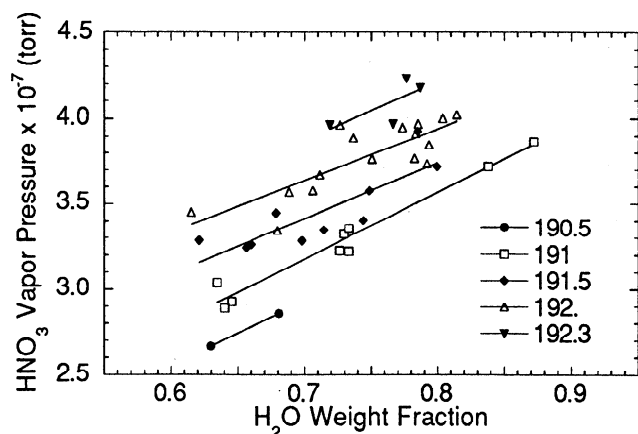


Figure 5. The variation of the HNO_3 vapor pressure as a function of the particle composition at a constant temperature. The symbols are the data points derived from the results shown in Figures 2a and 4 (see text for more detail).

$$P_{\text{HNO}_3}(\text{torr}) = [A(T) + B(T)f_w] \times 10^{-7} \quad (5a)$$

$$A(T) = 7988.2 - 84.386T + 0.22286T^2 \quad (5b)$$

$$B(T) = 1556.7 - 15.772T + 0.04T^2 \quad (5c)$$

It is important to note that (4) and (5) are only preliminary and are based on ER 2 in situ measurements near 55 mbar. In addition, both the measurement uncertainties and the possibility that the observed PSC could have a mixture of solid and liquid particles pose serious barriers in an accurate determination of the HNO_3 vapor pressure curve. Whether these expressions are valid at other locations or for different conditions can not be ascertained at this point. Future laboratory measurements are needed to accurately determine the vapor pressure behavior of HNO_3 over this assumed water-rich $\text{HNO}_3/\text{H}_2\text{O}$ metastable solid phase.

Marti and Mauersberger [1993] have shown that if the vapor ratio of H_2O to HNO_3 varies from 100 to 300, then a HNO_3 solid phase with a HNO_3 mole fraction of 0.25 to 0.125 is nucleated at ~ 192.5 K, respectively. Their results at 192.5 K can be fitted into a linear equation ($f_w = 0.36 + 1.02r$, where $r = [\text{H}_2\text{O}]_T / 1000[\text{HNO}_3]_T$). They concluded that for $r = 0.1$, NAT was formed and for $r = 0.3$, HNO_3 penta- or hexahydrate were probably formed [Marti and Mauersberger, 1994]. Using (4) and $r = 0.5$ (a typical mixing ratio for the ER 2 flight of January 20) our analysis of the ER2 data suggests $f_w = 0.79$ at 192.5 K. For the same condition ($r = 0.5$), Marti and Mauersberger's [1993] derived relation yields $f_w = 0.87$. Therefore, the weight percent composition calculated from the field data (4) is only about 10 % smaller than what is inferred from the only laboratory data available.

Measurement Uncertainties

In this section we investigate whether the measurement uncertainties would allow for ternary solutions to agree with the observed cloud data. The uncertainties in the measurements are illustrated as error bars in Figures 2a, 2b and 3, showing the relative error in the HNO_3 vapor concentration, HNO_3 aerosol content, and the aerosol volume, respectively. The relative error in the HNO_3 aerosol content ($[\text{HNO}_3]_{\text{aer}}$) is about ± 40 % [Kawa et al., 1992] and the error in the NO_y^* is about \pm

20 % [Loewenstein et al., 1993]. Thus the error in $[\text{HNO}_3]_{\text{gas}}$ is about ± 60 , which is estimated by adding the error in $[\text{HNO}_3]_{\text{aer}}$ to the error in NO_y^* , using propagation of errors and (3b). The error in the FSSP 300 volume is about ± 60 % [Baumgardner et al., 1992]. As shown in Figures 2b and 3, the derived $[\text{HNO}_3]_{\text{aer}}$ and the measured aerosol volume are independently inconsistent with ternary solutions, considering the range of measurement uncertainties. Hence within the limits of measurement uncertainties, a PSC cloud composed entirely of ternary solution droplets can not account for the observed cloud properties on January 20, 1989.

Previously, we were able to fit most of the PSC data on January 24, 1989 to the STS model within ± 20 % [Drdla et al., 1994]. Thus the lack of agreement between the STS model and the observed PSC data presented here is probably not due to the uncertainties in the measurements.

Discussion

In a recent study we used trajectories of air masses and the thermodynamic properties of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system to suggest that at least some of the H_2SO_4 aerosols were frozen in the air mass sampled by the ER 2 on January 20 while they were mostly liquid on January 24, when ternary solutions were observed [Tabazadeh et al., 1995]. The solid nature of aerosols on January 20 suggests that Type 1c PSCs may form via vapor deposition of HNO_3 and H_2O on frozen sulfate surfaces. Below, we describe a surface adsorption (or reaction) mechanism instead of a normal binary heterogeneous nucleation process for the formation of Type 1c PSCs in the stratosphere.

Previously, we applied the BET adsorption isotherm to estimate the number of adsorbed H_2O layers (~ 2) on the surfaces of acid particles present in the stratosphere [Tabazadeh and Turco, 1993]. If $f_w = 1$ in (4), then the adsorbed water layers are free of HNO_3 . However, from (4), f_w decreases as temperature is decreased and more HNO_3 is added to the adsorbed surface H_2O layers, this in turn may increase the amount of surface H_2O . For example, addition of potassium nitrate (KNO_3) to silver iodide (AgI) lattice enhances the adsorption of water vapor by AgI [Pruppacher and Klett, 1978]. This results because the number of hydrophilic (water-receptive) sites increase rapidly as more KNO_3 is added to the AgI lattice. In the stratosphere, as HNO_3 is added to the adsorbed water layers, the adsorption of H_2O vapor may be enhanced and this may result in the formation of a solid $\text{HNO}_3/\text{H}_2\text{O}$ film on a SAT particle. Also, heterogeneous chemical reactions of ClONO_2 with either HCl or H_2O on SAT may add more HNO_3 to the adsorbed water layers on the surface. Hence, the formation of this solid metastable phase may be initiated by a surface adsorption (or reaction) process instead of a normal heterogeneous nucleation mechanism.

This type of an adsorption/desorption process is mainly controlled by surface thermodynamics, and the equilibrium constant (Langmuir or BET) for this process can be approximated by the relations given by Tabazadeh and Turco [1993]. If the steady state surface concentration of H_2O and HNO_3 on a SAT particle are initially involved in the formation of solid PSCs particles, then all the sulfate particles (provided that they are solid) can grow to become $\text{HNO}_3/\text{H}_2\text{O}$ solid solutions. For example, Figure 6 illustrates the number density of particles measured by the FSSP 300 on January 20 [Dye et al., 1992]. On this day, it appears that most of the sulfate aerosols grew to sizes larger than $0.2 \mu\text{m}$ in radius (assuming a

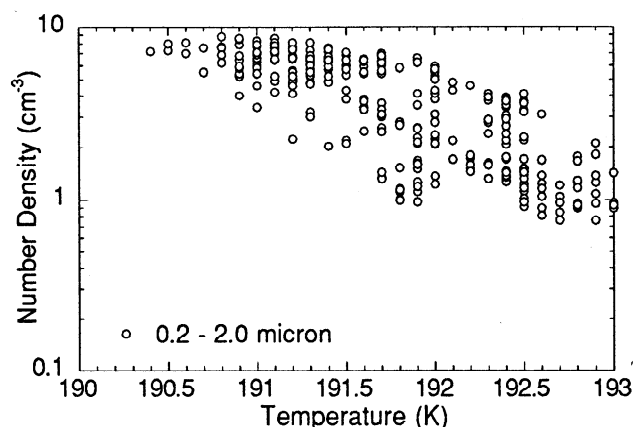


Figure 6. FSSP 300 particle number density for aerosols between 0.2 to 2 μm in radius plotted as a function of the ambient temperature for the ER2 flight of January 20, 1989 [Dye *et al.*, 1992].

number concentration of $\sim 10 \text{ cm}^{-3}$ for the background sulfate aerosols). This result may indicate that the mechanism responsible for the formation of January 20 PSC particles did not involve a nucleation barrier and therefore the majority of the existing aerosols grew. The same conclusion was reached for PSC observations on January 24. On this day, the cloud particles were ternary solutions formed from the dissolution of HNO_3 vapor in the preexisting $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution droplets [Tabazadeh *et al.*, 1994b]. In addition, nucleation in air masses having cooled rapidly by mesoscale temperature fluctuations, which occurs frequently in the Arctic, may also result in converting most of the existing sulfate aerosols into small PSC particles [Murphy and Gary, 1995]. Hence more work is needed in order to understand how solid particles containing HNO_3 are formed in the stratosphere. Both the surface adsorption process and rapid cooling of an air mass provide possible explanations for the activation of most of the background aerosols into solid HNO_3 -containing particles.

Up to this point, we have shown that the ER 2 data of January 20 is consistent with a water-rich solid condensate of HNO_3 . However, we have not considered the possibility of falling ice particles (Type II PSCs) coated with HNO_3 as an explanation for the ER2 data of January 20 [Wofsy *et al.*, 1990; Peter *et al.*, 1994]. Such particles are water rich, may have a variable HNO_3 composition and could result in air supersaturated with respect to HNO_3 (assuming a NAT composition for the PSC particles). Such factors are all consistent with the particle volume and composition data on January 20. However, as indicated above, most of the background aerosols participated in the formation of the observed PSC cloud on January 20 (Figure 6). If the volume growth was a result of HNO_3 -coated ice particles, then the particle number concentration should be significantly lower than the observations. The measured number concentration for Type 2 PSC particles (ice particles) in the stratosphere are in general less than 10^{-2} cm^{-3} [e.g., Hofmann and Deshler, 1989; Dye *et al.*, 1992]. Therefore, considering the particle number density, the possibility of the observed particles being HNO_3 -coated ice can be effectively ruled out.

As indicated above, the observed PSC on January 20 could have been composed of a mixture of liquid and water-rich HNO_3 -containing solid particles. In such a case, the variation of the aerosol composition with temperature could depend on the time required for vapor transformation to occur between the

water-rich solid particles and liquid ternary droplets. The composition shown in Figure 4 favors solid particles at higher temperatures and liquid particles at lower temperatures. This is plausible since the vapor pressure of HNO_3 over a ternary solution decreases rapidly with temperature decrease (see Figure 11 in Tabazadeh *et al.*, [1994a]). At higher temperatures, the HNO_3 vapor concentration is nearly unaffected by the uptake in the liquid droplets and this would allow for the formation of $\text{HNO}_3/\text{H}_2\text{O}$ metastable solid phases on the preexisting frozen sulfate cores. As the condensation temperature of $\text{HNO}_3/\text{H}_2\text{O}$ aqueous solutions is reached, the existing liquid droplets could remove a substantial fraction of HNO_3 from the gas phase and thus prevent the growth of the solid $\text{HNO}_3/\text{H}_2\text{O}$ metastable phases. Finally, if at colder temperatures the thermodynamic stability of a HNO_3 molecule is higher in a ternary solution as compared to in a solid metastable phase, then the HNO_3 in the water-rich solid particles could be transferred to the liquid particles, resulting in a cloud exhibiting more liquid-like properties with temperature decrease (see Figures 2-4).

Laboratory studies indicate that the initial condensate of a $\text{HNO}_3/\text{H}_2\text{O}$ solid phase formed by vapor deposition on a glass surface under stratospheric conditions is dilute in HNO_3 and grows richer in HNO_3 with time. For example, Marti and Mauersberger [1993] have shown that the initial condensate of H_2O and HNO_3 nucleated from a 300:1 vapor ratio of H_2O to HNO_3 roughly contained 12.5 mole % of HNO_3 in the solid phase. As this dilute condensate aged in the laboratory, a NAT (25 mole % HNO_3) composition was reached after 12 hours. The variation of composition with time observed during the experiments of Marti and Mauersberger [1993] may have been due to a vapor transformation process between a metastable higher hydrate phase and the stable NAT phase. During such experiments many small samples composed mainly of a higher hydrate were first nucleated on the walls of a glass cell. In time, some samples might have transformed into NAT or evaporated to provide more HNO_3 vapor for the growth of the NAT-nucleated samples. As a result the overall measured composition appeared to grow richer in HNO_3 with time. This time-dependent behavior would most likely continue until the majority of the initially nucleated dilute samples are transformed into NAT or evaporated off the walls. Similarly, the compositional variations of the observed PSC on January 20 illustrated in Figure 4 could have been due to the presence of a mixed cloud composed of higher hydrate particles and NAT aerosols. The vapor transformation between the higher hydrate particles and NAT aerosols would result in a PSC cloud that, once NAT nucleated, would grow richer in HNO_3 with time, noting that colder temperatures correspond to longer exposure times.

From the above discussion, NAT formation in the stratosphere may require a phase transformation step involving a higher hydrate. This type of a solid-solid (Type 1c \rightarrow Type 1a) phase transformation may provide a feasible pathway for the formation of large HNO_3 -containing aerosols in the stratosphere. Such aerosols were observed routinely by the DC 8 during the AASE 1 campaign from January 6 to January 31, 1989 [Browell *et al.*, 1990; Toon *et al.*, 1990a]. The mechanism proposed here for the formation of these large particles does not require temperatures below the ice frost point as suggested recently by Koop *et al.* [1995].

Laboratory studies show that aqueous aerosol solutions of HNO_3 with a mole ratio of 1:2.5 of HNO_3 to H_2O crystallize rapidly to NAT, whereas more water-rich samples remain

amorphous (M. Tolbert, personal communication, 1995). Other laboratory studies show that NAD crystallizes readily to NAT [Worsnop *et al.*, 1993]. However, according to ternary solution calculations [Tabazadeh *et al.*, 1994b], the highest possible HNO_3 concentration in a ternary droplet under stratospheric conditions is never rich enough in HNO_3 to allow for direct crystallization of either NAT or NAD from a ternary solution. A recent study indicates that nucleation of NAT or NAD particles from ternary solutions may initially require formation of a mixed $\text{H}_2\text{SO}_4/\text{HNO}_3$ ternary hydrate phase [Fox *et al.*, 1995]. The details of how NAT particles are nucleated from these metastable phases (higher hydrates of HNO_3 or mixed $\text{H}_2\text{SO}_4/\text{HNO}_3$ ternary hydrates) can not be inferred from this study and requires further field, laboratory, and modeling studies.

So far we have offered two explanations for the observed compositional behavior shown in Figure 4 involving mixtures of water-rich HNO_3 -containing solid particles with either ternary solution droplets or NAT (NAD) aerosols. However, the possibility that the observed PSC was a mixture of water-rich HNO_3 -containing particles, ternary solution droplets and NAT (or NAD) aerosols can not be excluded. The formation of a PSC cloud consisting of all particle types may require the presence of at least some frozen sulfate cores. The frozen cores could result in the formation of water-rich HNO_3 -containing solid particles and the liquid cores could grow into ternary solution droplets. As described above, some of the water-rich solid particles may convert to NAT (or NAD) aerosols. The cloud composition composed of all three particle types would grow richer in HNO_3 with time due to vapor transformation from the ternary droplets and water-rich solid particles to the NAT nucleated aerosols. The only combination of particles that is inconsistent with the data would be a mixture of ternary solution droplets and NAT (or NAD) aerosols since the water content of this mixture would be less than that of a ternary solution (see Figure 4).

Conclusions

In this work, we suggest a metastable HNO_3 water-rich solid phase (Type 1c PSCs) as a possible composition for some observed Type 1 PSC particles. In support of this idea, we investigated the ER 2 PSC data of January 20, 1989, and showed that this data can not be explained assuming that the observed cloud particles were entirely composed of NAT, NAD, or ternary solutions. We also discussed a few laboratory measurements, which agreed with our main conclusions that these metastable HNO_3 -containing solid phases are water-rich and that the HNO_3 vapor pressure over such a solid surface is relatively high [Hanson, 1992; Marti and Mauersberger, 1993; Iraci *et al.*, 1995]. A surface adsorption (or reaction) process was discussed as a possible mechanism for the formation of solid Type 1c PSC particles on frozen sulfate cores. Further, we presented arguments to suggest that the observed PSC on this day could have been a mixture of particles composed of water-rich HNO_3 -containing particles with ternary solution droplets, and/or NAT (or NAD) aerosols, whereas the possibility of ternary solution droplets mixed in with NAT (or NAD) particles was effectively ruled out.

Laboratory data are currently lacking on the thermodynamic properties of these metastable $\text{HNO}_3/\text{H}_2\text{O}$ solid phases, such as composition and vapor pressure, to investigate whether they can form under polar stratospheric conditions. We hope the results discussed here encourage some laboratory groups to

further study the physical and chemical properties of metastable $\text{HNO}_3/\text{H}_2\text{O}$ solid phases, especially in establishing the appropriate thermodynamic phase boundaries.

Finally, we speculate that once solid Type 1c PSCs nucleate in the air mass, in time they might transform into NAT or NAD particles. Once a few NAT or NAD particles are nucleated, they could grow at the expense of the remaining Type 1c (or Type 1b) particles that are not activated into NAT or NAD because of the vapor pressure difference between these coexisting HNO_3 -containing phases. This would allow NAT or NAD particles to grow relatively large. The sedimentation of these large particles would result in denitrification, which directly affects the ozone chemistry in the stratosphere [Salawitch *et al.*, 1989; Toon *et al.*, 1990b].

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